MULTIPLE REACTION SCHEME MODELLING*

II Parameter Selection and Re-examination of Mutually Independent First Order Reactions

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A simple procedure whereby the energies of activation and pre-exponential factors of the individual reactions, of any kinetic model, comprising a wide variety of multiple reaction sets, is described. The sets belong to one of three classes, such that the single extent of reaction—temperature curves diverge, converge or are equally spaced at one prescribed temperature. The method has been applied to sets of first order reactions, which yield effective n^{th} order reactions with the order 'n' varying from ~ 0.6 to ~ 3.0. Variations in Friedman iso-conversional reaction kinetics analytical data are indicative of the designed reaction complexity.

A simple approach to the selection of the kinetic parameters of the individual members of a set of reactions used to model multiple thermal processes is described. A set of extent and rate of reaction curves are obtained by moving master curves, generated under constant heating rate conditions, along the temperature axis by predefined intervals. The kinetic parameters of each member reaction are obtained by Arrhenius analysis. By appropriate choice of the temperature interval, a wide range of individual reactions may be generated. They are characterized in terms of the values of the extent of reaction at the temperature corresponding to the maximum rate of the master reaction. Three classes of multiple sets are considered, in which the relative spacing between the several extent of reaction–temperature curves at this temperature change by equal, incremental and decremental amounts. The procedure, although quite general, has been applied only to sets of first order reactions, which yield singular effective n^{th} order reactions, in which 'n' can vary from ~ 0.6 to ~ 3.0. The single reaction activation energies may vary randomly or change by integral amounts. The dependence of the order of the overall reaction,

and its global paramaters on the three classes of multiple sets is described. Significant variations in the Friedman-derived isoconversional kinetic parameters can be correlated to the complexity of the various multiple sets.

Many examples of solid state reactions exist where it is highly probable that monitored physico-chemical data reflects the overall effect of a number of singular reactions proceeding in several ways, independently, competitively and/or consecutively. Of thermoanalytical interest, fossil fuel pyrolyses, low temperature, slow oxidative degradations of organic compounds with several susceptible functional groups, and thermal decompositions at different crystal faces or grain boundaries of a single substance are potential candidates. It has been reported in a recently abstracted publication that Kalinenko et al. [1] have considered fifty eight simultaneous reactions in an investigation of the pyrolysis and steam gasification of coal. In a study of the pyrolysis of a bituminous coal, Solomon et al. [2] list first order kinetic parameters for seventeen functional group degradations. Generally, attempts at modelling the kinetics of multiple solid state reactions have been sporadic. Essenhigh [3] has summarized the various kinetic schemes proposed for the analysis of coal pyrolysis data. Some success in curve fitting experimental results, particularly non-isothermal thermogravimetric data, has been achieved by employing a model of a set of individual first order reactions with a Gaussian distribution of activation energies or both energies of activation and pre-exponential factors. See Elder [4], Elder and Harris [5] or Elder and Reddy [6] for pertinent references. There are a number of limitations to this approach [4]. The characteristics of the overall reaction resulting from a combination of both mutually independent, and competitive single, first order reactions have been investigated by the author [4]. Dowdy [7, 8] has used a slightly different approach in attempting to describe the kinetics of the overall reaction by introducing an 'instantaneous mean activation energy'.

The computer modelling program previously introduced [4] has a number of drawbacks. Although it enabled the effective reactions at different heating rates, resulting from a set of single reactions with relatively close-valued kinetic parameters, to be analysed by various means, like the Gaussian distribution models, only first order reactions could be considered. The major limitation however, lay in the selection of the single reaction parameters. In order to be able to generate a continuous, effective extent of reaction–temperature curve with a single maximum reaction rate, a trial and error selection procedure has had to be used. This is very tedious and time-consuming, particularly so when attempts are made to employ large numbers of single reactions in the model. This essentially defeats the purpose of using the computer for modelling. Furthermore, one could not easily examine the consequences of using single reaction kinetic parameters which result in asymmetrically positioned extent and rate of reaction–temperature curves.

In the past few years, there has been a growing realization of the wide applicability of the Friedman approach to kinetic analysis [9]. In principle, the iso-conversion method uses multiple heating rate data, and obviates the need for a prior establishment of the reaction kinetic model. Its use has been advocated by both the author [10] and by Ozawa [11] for single reactions. It has also been employed in analysing multiple reaction data [4, 8], and there are indications that variations in the values of Friedman parameters with conversion can assist in the elucidation of the complexity of multiple reaction schemes. Experimentally, it has been used in analysing coal [6, 12] and mineral [13] degradation data.

The kinetic modelling program KINMOD [4], has now been extended to cover a number of solid state models [14], selected from those listed by Brown, Dollimore and Galwey [15], and also by Šesták [16]. Furthermore, calculations may now be performed over the appropriate temperature range at any heating rate with a 0.2 °C interval between computed extent and rate of reaction data points. Elder and Reddy [6], and Elder [12] have shown that although limited to the intermediate stage of the overall degradation, coal pyrolysis data may be fitted successfully, albeit empirically, to the nth order rate equation (cf. the Koch caveat [17]). Calculations, to be communicated at a later date, have shown that the effective reaction resulting from certain multiple sets constructed from single, solid state model reactions [14], can be fitted to the nth order law, just as in the case of single reactions [10]. Therefore, it is considered appropriate and necessary to re-examine the characteristics of nth order overall data generated from the most simple single reactions, namely, those of first order.

A simple approach to the selection of the individual, first order reaction kinetic parameters will be described. It will be used to generate parameters for use in the modelling program, KINMOD, to examine the consequences of using reactions which result in a skewed distribution of extent of reaction–temperature curves, on the order of the overall reaction, and on the global kinetic parameters obtained by Friedman and Kissinger analyses of the modelled non-isothermal data.

Parameter selection

Dollimore, Gamlen and Taylor [18] have discussed the use of the temperature-dependent pre-exponential factor, $A \cdot T^m$, in the rate equation. In this study, all single reactions in the multiple set, and the effective reaction, are assumed to obey the transition state law, namely $m = 1$.

The kinetic parameters, activation energy, E_1, and pre-exponential factor, A_1, of the first reaction in the set, the master reaction, are first chosen. The extents and rates of reaction as functions of temperature are calculated using equation (1) and its integral form [14], equation (2). The remaining individual reaction parameters in

Table 1 Calculation of E and A Values; Model F1; $m = 1$; 10.0 C/min

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5% Incremental Change in Curve Spacing   alpha(last) = 0.100* alpha (first)

E(kJ/mol)	A (K. min)$^{-1}$	E (kJ/mol)	A (K. min)$^{-1}$	E (kJ/mol)
220.00	1.2500E + 12	224.59	1.8556 + 12	229.89
ln A = k1*	E + k2		k1 = 8.205E-02	k2 = 9.817E + 00
E (kJ/mol)	A (K. min)$^{-1}$	E (kJ/mol)	A (K. min)$^{-1}$	E (kJ/mol)
220.00	1.2500E + 12	230.00	4.4756E + 12	240.00
	T(max) = 478.4 C		T(max) = 485.4 C	T(max) = 493.6 C
ln A = k1* E + k2			k1 = 1.154E-01	k2= 2.530E + 00

20% Equal Change in Curve Spacing   alpha(last) = 0.200* alpha (first)

E (kJ/mol)	A (K. min)$^{-1}$	E (kJ/mol)	A (K. min)$^{-1}$	E (kJ/mol)
220.00	1.2500E + 12	224.28	1.7898E + 12	229.20
ln A = k1*	E + k2		k1 = 8.273E-02	k2 = 9.662E + 00
E (kJ/mol)	A (K. min)$^{-1}$	E (kJ/mol)	A (K. min)$^{-1}$	E (kJ/mol)
220.00	1.2500E + 12	230.00	4.5471E + 12	240.00
	T(max) = 478.4 C		T(max) = 485.1 C	T(max) = 492.5 C
ln A = k1* E + k2			k1 = 1.124E-01	k2 = 3.248E + 00

15% Decremental Change in Curve Spacing alpha (last) = 0.522* alpha (first)

E (kJ/mol)	A (K. min)$^{-1}$	E (kJ/mol)	A (K. min)$^{-1}$	E (kJ/mol)
220.00	1.2500E + 12	223.23	1.6476E + 12	226.07
ln A = k1*	E + k2		k1 = 8.396E-02	k2 = 9.384E + 00
E (kJ/mol)	A (K. min)$^{-1}$	E (kJ/mol)	A (K. min)$^{-1}$	E (kJ/mol)
220.00	1.2500E + 12	230.00	4.9701E + 12	240.00
	T(max) = 478.4 C		T(max) = 483.4 C	T(max) = 487.8 C
ln A = k1* E + k2			k1 = 1.388E-01	k2 = −2.688E + 00

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the prescribed set are obtained by moving the extent and rate of reaction–temperature curves of the first reaction, the master curves, along the temperature axis, by an amount ΔT_i, such that each α_i at the temperature, $T_1(\max)$ of the maximum rate, $\dot{\alpha}_1(\max)$ of the master reaction, is given by equation (3). At this temperature, the separation between the first and last member of the set is given by equation (4), with $0 < f < 1$. S_1 and S_2 depend upon the relative spacing, x, between the curves at $T_1(\max)$, where x is defined by equation (5). If $x < 1$, the curves converge. This is referred to as decremental spacing. If $x > 1$, the curves diverge, and one has incremental spacing. If the curves are equally spaced, $x = 1$. With the following provisos, $1 < j < L$, where L is the number of members in the set, and $0 < y < 1$, then S_1 and S_2 are given by equations (6)

$$\mathrm{d}\alpha_1/\mathrm{d}t = A_1 \cdot T \cdot \exp(-E_1/RT) \cdot (1 - \alpha_1) \qquad (1)$$
$$-\ln(1 - \alpha_1) = A_1/\beta \cdot (E_1/R)^2 \cdot p_1(E_1/RT) \qquad (2)$$

A (K. min)⁻¹	E (kJ/mol)	A (K. min)⁻¹	E (kJ/mol)	A (K. min)⁻¹
2.8711E + 12	237.43	5.3666E + 12	253.31	1.9320E + 13
k2 = 9.817E + 00	CC = 0.9999		5 regression pairs	
A (K. min)⁻¹	E (kJ/mol)	A (K. min)⁻¹	E (kJ/mol)	A (K. min)⁻¹
1.4639E + 13	250.00	3.9463E + 13	260.00	5.4496E + 13
T(max) = 493.6 C	T(max) = 505.0 C		T(max) = 528.4 C	
k2 = 2.530E + 00	CC = 0.9984		5 regression pairs	

A (K. min)⁻¹	E (kJ/mol)	A K. min)⁻¹	E (kJ/mol)	A (K. min)⁻¹
2.7261E + 12	235.24	4.4884E + 12	244.50	9.4698E + 12
k2 = 9.662E + 00	CC = 0.9999		5 regression pairs	
A (K. min)⁻¹	E (kJ/mol)	A (K. min)⁻¹	E (kJ/mol)	A (K. min)⁻¹
1.5554E + 13	250.00	4.7145E + 13	260.00	1.0735E + 14
T(max) = 492.5 C	T(max) = 501.7 C		T(max) = 515.6 C	
k2 = 3.248E + 00	CC = 0.9966		5 regression pairs	

A K. min)⁻¹	E (kJ/mol)	A (K. min)⁻¹	E (kJ/mol)	A (K. min)⁻¹
2.0828E + 12	228.75	2.6060E + 12	231.31	3.2380E + 12
k2 = 9.384E + 00	CC = 1.0004		5 regression pairs	
A (K. min)⁻¹	E (kJ/mol)	A (K. min)⁻¹	E (kJ/mol)	A (K. min)⁻¹
1.9941E + 13	250.00	8.0160E + 13	260.00	3.2166E + 14
T(max) = 487.8 C	T(max) = 491.9 C		T(max) = 495.8 C	
k2 = −2.688E + 00	CC = 1.0000		5 regression pairs	

$$\alpha_i = \alpha_1 \cdot (1 - S_1 \cdot S_2) \tag{3}$$

$$\Delta\alpha_{1-L} = \alpha_1 \cdot (1 - f) \tag{4}$$

$$\alpha_{i+1} - \alpha_{i+2} = x \cdot (\alpha_i - \alpha_{i+1}) \tag{5}$$

Decremental: $\quad S_1 = (1-f)/\Sigma_0^{L-2}(1-y)^i \quad\quad S_2 = \Sigma_0^{j-2}(1-y)^i$

Incremental: $\quad S_1 = (1-f)/\Sigma_0^{L-2}(1+y)^i \quad\quad S_2 = \Sigma_0^{j-2}(1+y)^i \tag{6}$

Equal: $\quad\quad S_1 = (1-f)/(L-1) \quad\quad\quad S_2 = j$

A fortran program, PARCAL, has been developed by incorporating equations (3)–(6) into the Arrhenius section of the original modelling program, KINMOD. Using equations (1) and (2), α_1 and $\dot{\alpha}_1$ are generated for the master reaction, and the start and end temperatures, corresponding to α_1 varying from 0.001 to 0.999, are calculated. An Arrhenius analysis is then performed on this data, with the start temperature increased by ΔT_i, for each member of the set. The program also enables the calculation of a set of A_i values for integral values of E_i, separated by a

fixed amount, ΔE. This calculation is performed using equation (2a), a generalized version of (2).

$$A_i = \frac{\ln[1 - \alpha_i(\max)].}{(E_i/R)^2 \cdot p_1[E_i/RT_i(\max)]} \tag{2a}$$

where $\alpha_i(\max)$ and $T_i(\max)$ are obtained from the previous Arrhenius analysis of the α_i, $\dot{\alpha}_i$ data. As is to be expected, the generated E_i, A_i set, in both cases, fit the compensation law, equation (7)

$$\ln A_i = k_1 \cdot E_i + k_2 \tag{7}$$

It should be pointed out that the E_i, A_i values are dependent upon the heating rate chosen to generate the α_i, $\dot{\alpha}_i$ data set. For the master curve, $E_1 = 220$ kJ/mol and $A_1 = 1.25 \cdot 10^{12}$ deg^{-1} min^{-1}, will be used throughout.

Table 1 shows typical program output for three selected five-member models, calculated at 10 deg/min. For integral E_i values, a separation of 10 kJ/mol was chosen. The temperature-shifted complement of the extent of reaction-temperature curves are shown in Figure 1. The first data set are for a model in which the curve spacing at 478.4°, ($T_1(\max)$), increases by 5% with $\alpha_5 = 10\%$ of α_1. The second set refers to equally spaced curves with $\alpha_5 = 20\%$ of α_1. The third set is for a model in which each α_i at 478.4° is 85% of its predecessor. The dashed lines show the course of the resulting effective reaction, assuming mutual independence of the single members of the multiple set. The magnitude of the temperature shifts for each member is given by the difference, $T_i(\max) - T_1(\max)$ in Table 1. The overall reaction Arrhenius kinetic parameters, 'E_A, A_A, n', for these models are given in Table 2.

As previously described, Arrhenius analysis of the effective reaction data is performed by linear regression of the logarithmic form of the rate equation [4]. The regression is terminated if a continual limiting deviation from linearity is detected. Here, strict control over the regression is maintained by setting the limit at 1%. If the incorrect reaction order is used in the rate equation, deviations are detected at fairly low values of the effective extent of reaction. For example, for the overall reaction shown in Figure 1A, if the data is analysed as first order, the regression terminates at $\alpha = 0.255$, as indicated by the vertical arrow at 471°, and one obtains $E_A = 222.8$ kJ/mol and $A_A = 9.22 \cdot 10^{11}$ deg^{-1} min^{-1}. On the other hand, when the correct reaction order, namely, 1.67, is used, the regression terminates at $\alpha = 0.84$, as shown by the vertical arrow at 521°, and one obtains the more correct parameter values given in Table 2. In this particular case, the differences are not too large. However, it is very important that correct reaction orders be used in Arrhenius analyses, since for some models regression termination occurs at low values of α for a completely different reason. As will be seen, this behavior is related to an observed, significant variation in the Friedman-derived kinetic parameters with extent of reaction.
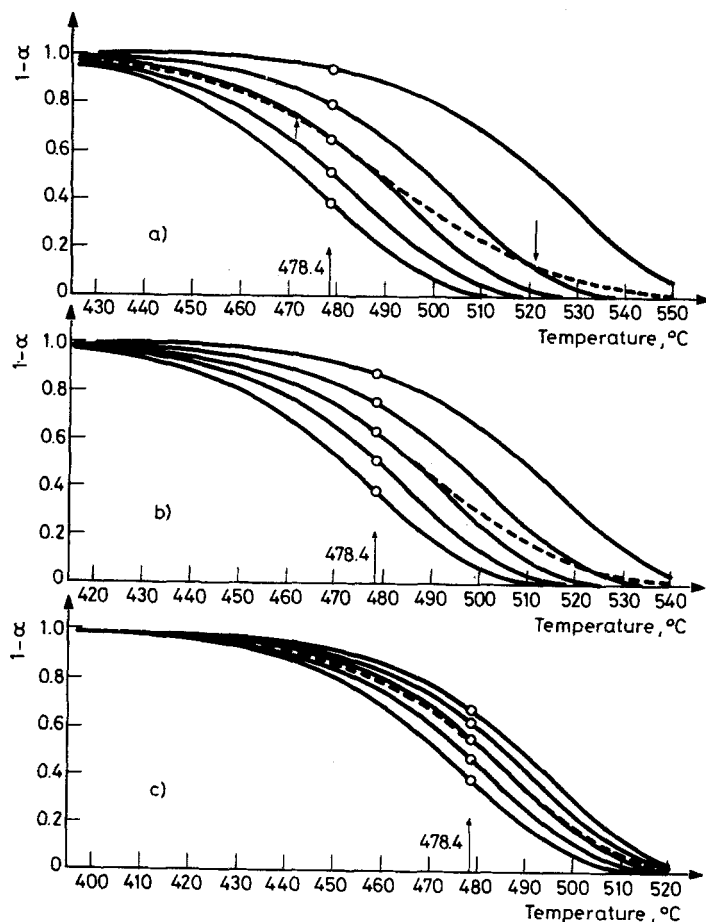
Fig. 1 Complement of extent of reaction *vs.* temperature. 5 member set. calculated at 10 deg/min, $T_1(\max) = 478.4$ °C. a: 5% incremental spacing, $\alpha_5 = 0.1 \cdot \alpha_1$, b: 20% equal spacing, $\alpha_5 = 0.2 \cdot \alpha_1$, c: 15% decremental spacing $\alpha_5 = 0.522 \cdot \alpha_1$

Figure 2a shows the $1 - \alpha$ *vs.* T curves at 150 deg/min for the five-member set with $\alpha_5 = 0.1$. α_1, and 5% incremental spacing, and the effective reaction, $n = 1.65$, analogous to Figure 1a.. The circles represent the $1 - \alpha$ values generated by the modelling program, using the integral E_i, A_i data with $\Delta E = 9$ kJ/mol. As can be seen, the agreement is excellent. Provided that the spread of the E_i values generated by the two procedures in program PARCAL are not too different, such agreement is generally the case. Figure 2b shows the effective $1 - \alpha$ *vs.* T curves at three widely separated heating rates, 1, 10 and 100 deg/min, using the 150 deg/min generated E_i, A_i data sets. The heating rate at which the individual E_i, A_i values are generated has

Table 2 Mutually independent model kinetic parameters

Heating rate	Spacing	Arrhenius analyses					
		Variable E_i and A_i Values			Set E_i and Variable A_i Values		
		E_A, kJ/mol	A_A, (deg. min)$^{-1}$ · 10^{-12}	n	E_A, kJ/mol	A_A, (deg. min)$^{-1}$ · 10^{-12}	n
10 deg/min ¶	5% Incremental	227.8	2.33	1.67	230.9	3.79	1.65
	20% Equal	225.7	1.69	1.37	229.4	2.98	1.34
	15% Decremental	224.1	1.60	1.07	232.0	5.62	1.03
1 deg/min*	5% Incremental	228.6	2.68	2.02			
10 deg/min*		227.1	1.95	1.85			
100 deg/min*		226.6	1.74	1.69			
150 deg/min*		226.8	1.78	1.65			

Kissinger analysis (1–150 deg/min)

E_K, kJ/mol	A_K (deg. min)$^{-1}$ · 10^{-12}
223.4	1.10

Friedman analyses ($\alpha = 0.05–0.85$)

E_F, kJ/mol	A_F (deg. min)$^{-1}$ · 10^{-12}
224.9–220.0	1.30–0.74

¶Single reaction parameters generated at 10 deg/min
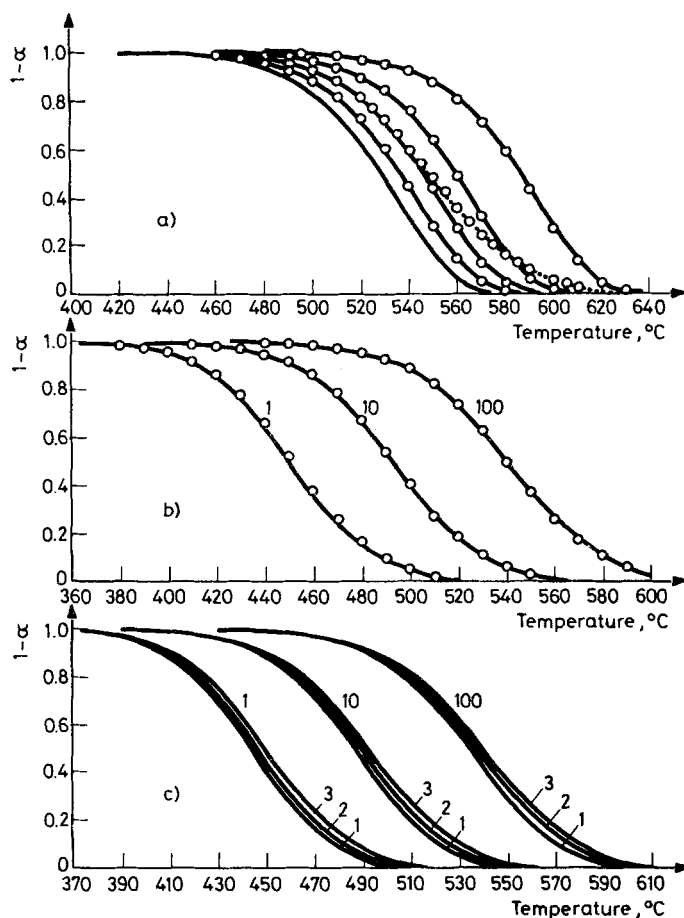*Single reaction parameters generated at 150 deg/min

Fig. 2 Complement of extent of reaction *vs.* temperature. 5 member set, $\alpha_s = 0.1 \cdot \alpha_1$. a: single and effective reactions at 150 deg/min, b: effective reactions at 1, 10 and 100 deg/min from 150 deg/min single reaction data, c : effective reactions at 1, 10 and 100 deg/min from single reaction data at 1, 10 and 100 deg/min (1, 2, 3)

a small effect on these overall reaction curves, as shown in Figure 2c. Here, the numbers (1, 2, 3) adjacent to each curve, indicate the heating rate (1, 10 and 100 deg/min) at which the E_i, A_i data set was generated.

In examining the consequences of varying x, f and L, and therefore, S_1 and S_2, equations (3)–(6), on the kinetic parameters and order of the overall reaction, it has been found most suitable to generate the single reaction, first order parameters at the highest heating rate to be used in the Friedman and Kissinger analyses. Here, 150 deg/min has been used throughout. The kinetic parameters for the five

individual reactions comprising the set, shown in Figure 2A, were generated at this heating rate (E_i, A_i: 220.0, $1.250 \cdot 10^{12}$; 224.9, $1.848 \cdot 10^{12}$; 230.7, $2.895 \cdot 10^{12}$; 238.7, $5.345 \cdot 10^{12}$; 255.9, $1.956 \cdot 10^{13}$). They are very close to those values generated at 10 deg/min, shown in Table 1. The kinetic parameters for the effective reactions, in Figures 2a and 2b, resulting from Arrhenius analyses at the four indicated heating rates, Kissinger analysis of data generated at ten heating rates, 1 — 150 deg/min, and Friedman analyses from 5 — 85% extent of reaction, are given in Table 2.

Multiple scheme effective reaction orders

The total relative separation between the first and last member $1 - \alpha$ vs. T curves of a multiple set at T_1(max) may be expressed by the ratio $\alpha_L / \alpha_1 = f$. Figure 3 shows how the effective reaction order varies with this ratio for a five, ten, twenty-five and fifty member set, with equal, 5% incremental and decremental relative spacing. The circles on the five member curves represent the values obtained for the E_i, A_i data sets with equally separated E_i integral values. ΔE varies from 2.5 kJ/mol at $f = 0.6$, through 7.6 kJ/mol at $f = 0.15$ to 13.6 kJ/mol at $f = 0.025$. Similar agreement is obtained with the other multiple sets. As the envelope encompassing the extreme members of a set increases, so does the order of the effective reaction. There is however, a limit to the size of the envelope. One finds that at $f \leqslant 1\%$, second and third
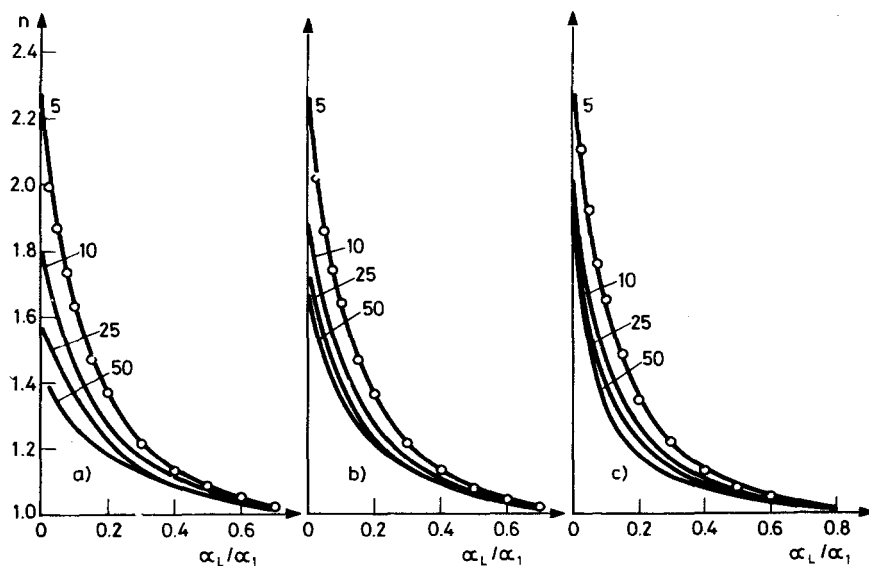

Fig. 3 Effective reaction order 'n' vs. α_L / α_1. 5, 10, 25 and 50 members sets. a: 5% incremental, b: equal, c: 5% decremental spacing
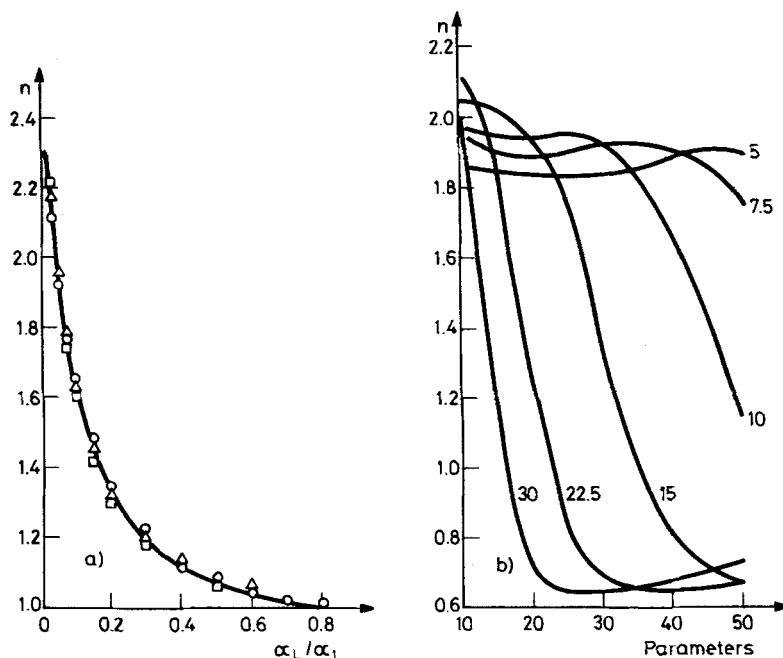
Fig. 4 Effective reaction order 'n' $- x\%$ Decremental Spacing. a: $n.$ $vs.$ α_L/α_1, 5 member set, $x = 5$ (—), 10 (○), 20 (△), 30 (□). b: n $vs.$ number of member parameters, $\alpha_L = 0.01 \cdot \alpha_1$, $x = 5$, 7.5, 10, 15, 22.5, 30

peaks begin to appear in the $\dot\alpha - T$ curve at high α, ($\alpha > \sim 0.9$), particularly in multiple sets with incremental spacing.

Regression termination in the Arrhenius analysis of the overall reaction of a multiple set, and therefore, the E_A, A_A values obtained, is dependent on the model design. For equally and incrementally spaced $1 - \alpha$ $vs.$ T curve models, for low number member sets, $L \leqslant 5$, at $f \leqslant 10\%$, regression termination at the 1% deviation level occurs at $\alpha_{end} \sim 0.4$. α_{end} increases with the number of members, L. Thus, for $L = 50, f = 5\%$, $\alpha_{end} \leqslant 0.8$. For decrementally spaced models, an opposite effect is observed. For $L = 50$, at $f = 10\%$, $\alpha_{end} \sim 0.3$, but as L decreases, so α_{end} increases. Thus, for $L = 5$, $\alpha_{end} \sim 0.7$.

For low number member multiple sets, variation in the magnitude of the relative spacing, x, has little effect on the $n - \alpha_L/\alpha_i$ relationship, a demonstrated in Figure 4A, for 5–30% decrementally spaced, five member sets. In such a model, if both x and L increase, odd effects are observed, as shown in Figure 4b. Analogous incrementally spaced multiple sets do not exhibit this behavior. In the case of $\alpha_L/\alpha_1 = 1\%$, for 5% decrementally spaced curves, 'n' changes very little with increase in L. As x increases

to 30%, so there is a sudden decrease in n as L increases. Thus, while a ten member set with 30% decremental spacing yields an effective reaction with $n \sim 2$, a twenty member set with the same relative spacing results in an overall reaction with $n \sim 0.7$. For the analogous multiple sets with 30% incremental spacing, the effective reaction orders are $n \sim 1.60$ and $n \sim 1.33$, respectively. For both the decrementally spaced multiple sets, in which the kinetic parameters for the final member are 285.9 kJ/mol $1.857 \cdot 10^{14}$ deg^{-1} min^{-1}, Friedman analyses of the overall reaction data, generated by program KINMOD at ten heating rates, covering the range, 1–150 deg/min, showed steadily increasing kinetic parameters with increase in the extent of the overall reaction. For the ten member set, the energy of activation and pre-exponential factor varied from $E_F = 229.7$ to 253.8 kJ/mol, and $A_F = 1.342 \cdot 10^{12}$ to $5.652 \cdot 10^{13}$ deg^{-1} min^{-1} for 5–90% extent of reaction. In the case of the twenty member set, the variation is in the same direction, but larger. Over the range, 5–95% extent of reaction, E_F varies from 235.1 to 311.8 kJ/mol, and A_F changes from $1.485 \cdot 10^{12}$ to $2.924 \cdot 10^{15}$ deg^{-1} min^{-1}. When the curve spacing diverges, one has a completely different state of affairs, the Friedman parameters do not change drastically. At 150 deg/min, the reaction orders for the ten and twenty member sets are 1.60 and 1.57, respectively. For the ten member set, the Friedman-derived energies of activation and pre-exponential factors decrease sligthly from 223.6 to 220.0 kJ/mol, and 1.322 to $1.193 \cdot 10^{12}$ deg^{-1} min^{-1} for 5–50% extent of reaction. In the next 45% extent of reaction, the parameters increase slightly to 253.2 kJ/mol and $1.396 \cdot 10^{13}$ deg^{-1} min^{-1}. In the case of the twenty member set, for 5–60% extent of reaction, the changes are similar. The energy of activation decreases from 222.1 to 220.8 kJ/mol, and the pre-exponential factor decreases from 1.289 to $1.181 \cdot 10^{12}$ deg^{-1} min^{-1}. In the next 25% extent of reaction, the parameters increase very slightly to 225.7 kJ/mol, and $2.010 \cdot 10^{12}$ deg^{-1} min^{-1}.

As a result of these observations, a more detailed study into the variation of Friedman-derived kinetic parameters with model design was undertaken. A series of calculations were performed for five to fifty member multiple sets with various incremental, decremental and equal spacing between the $1 - \alpha$ vs. T curves. In each case, as a matter of course, the α_{max}, $\dot{\alpha}_{max}$, T_{max} data was also subjected to Kissinger analysis.

Friedman and Kissinger analysis of multiple reaction data

In what follows, since generally the natural logarithms of the pre-exponential factors follow the direction of the variation in the activation energies, for brevity, only the latter data will be presented for discussion.

Figure 5 shows the variation in E_F with α for equally spaced sets, and those with 5% incremental and decremental spacing. In all cases, $\alpha_L = 10\%$ of α_1, and the
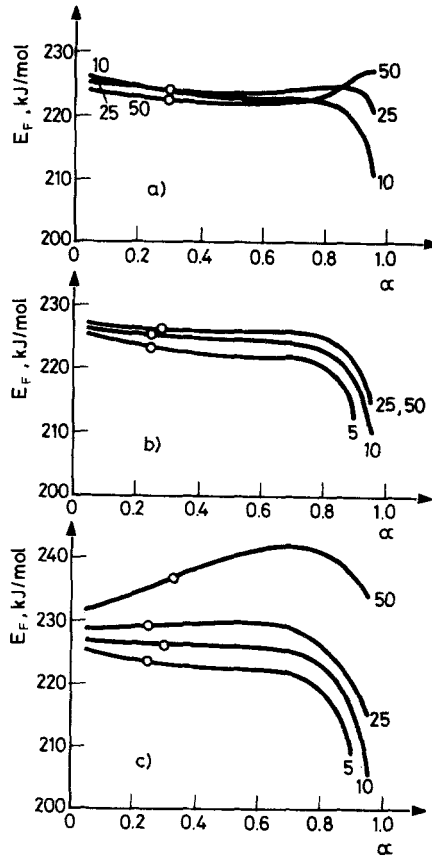
Fig. 5 Friedman activation energy *vs.* extent of reaction. $\alpha_L = 0.1 \cdot \alpha_1$, $E_L = 255.9$ kJ/mol, 5, 10, 25, 50 member sets. a: 5% incremental, b: equal, c: 5% decremental spacing. Kissinger values ($\bigcirc$)

activation energy of the last member in all sets considered is 255.4 kJ/mol. The numbers adjacent to the curves indicate the number of members in the sets considered, and the circles indicate the Kissinger analysis derived values. As can be seen, for the equally and incrementally spaced sets, over 85% of the extent of reaction, there is little change in E_F with either number of members in the set, or extent of reaction. Note also the closeness of the Friedman and Kissinger derived values, a point raised in the case of single reactions [10]. In the case of decrementally spaced sets, two facts emerge. First, in the range $0 < \alpha < 0.7$, at any extent of reaction, there is a significant increase in E_F as the number of members in the sets, L, increases. Secondly, the overall character of the variation with extent of reaction changes with increase in L.

By widening the envelope between the first and last single reaction $1 - \alpha$ *vs.* T
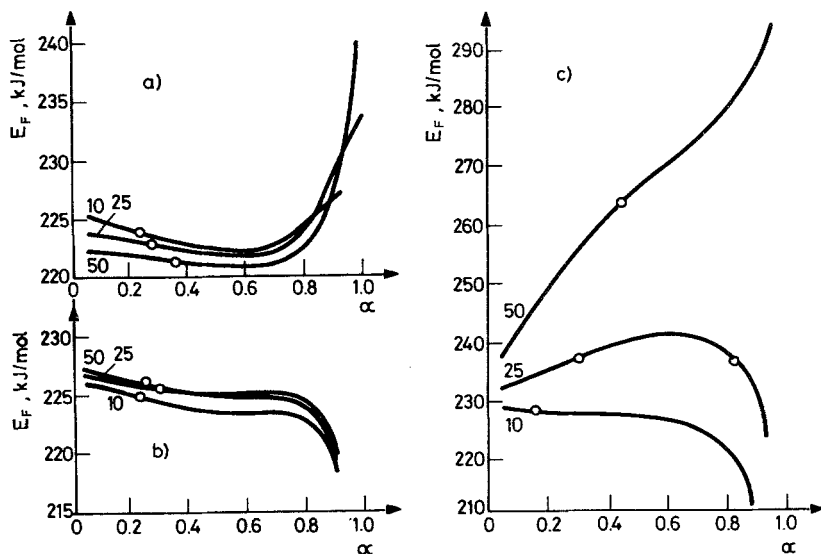
Fig. 6 Friedman activation energy *vs.* extent of reaction. $\alpha_L = 0.05 \cdot \alpha_1$, $E_L = 265.2$ kJ/mol, 10, 25, 50 member sets. a: 10% incremental, b: equal, c: 10% decremental spacing. Kissinger values (O)

curves, and increasing the magnitude of the relative change in curve spacing, these observed effects are enhanced. Thus, in figure 6 are shown the E_F (and E_K) *vs.* α curves for three multiple sets with ten, twenty-five and fifty members, respectively, with equal, 10% incremental and decremental spacing, and $\alpha_L = 5\%$ of α_1, $E_L = 265.2$ kJ/mol. Again, little change is seen in the equally spaced curves, and only minor changes in the $0.85 < \alpha < 1.0$ region of the incrementally spaced. The really marked effects, once again, are associated with decrementally spaced multiple sets. In Figure 7, analogous curves to those in figure 6c are shown. The relative single reaction $1 - \alpha$ *vs.* T curve spacing is the same, but the first to last member curve envelope has been expanded to $\alpha_L = 1\%$ of α_1, with $E_L = 285.9$ kJ/mol.

In all the examples considered up to this point, the individual $1 - \alpha$ *vs.* T curves have been separate, even if, in certain cases, quite close. Correspondingly, the E_i, A_i values for all sets have been different. If models with $x \geqslant 15\%$, and $L \geqslant 40$, are considered, one obtains single reaction E_i, A_i values which are too close to be distinguished from those arising as a result of the variance of the linear regression. The extent of reaction curves are too close to separate at the lower and upper regions of the temperature interval, for incremental and decremental spacing, respectively. This manifests itself in multi-stepped effective extent of reaction (i.e. multi-peaked reaction rate), curves, and is more evident with the incrementally spaced multiple reaction models.

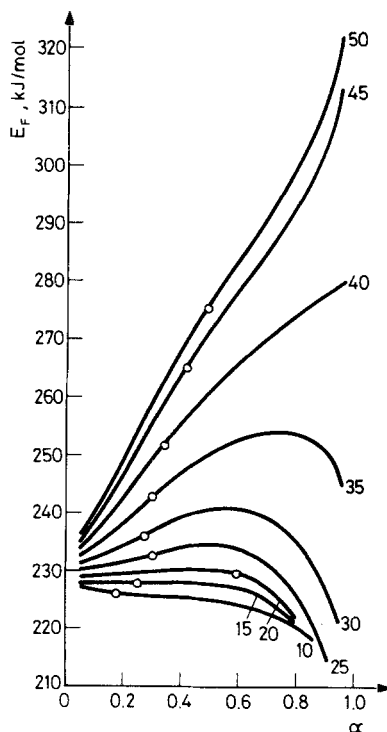It is pertinent, at this point, to consider the multiple Arrhenius, ($m = 0$), models,

Fig. 7 Friedman activation energy *vs.* extent of reaction. $\alpha_L = 0.01 \cdot \alpha_1$, $E_L = 285.9$ kJ/mol, 10% decremental spacing. 10, 15, 20, 25, 30, 35, 40, 45 and 50 member sets. Kissinger values ($\bigcirc$)

recently discussed by Dowdy [8]. The five, nine-member, first order sets ($E_i = 180 - 220$, $\Delta E = 5$ kJ/mol), have been analysed as mutually independent. Both the under-compensated set, (case 4, ln $A_i = 54.85 - 0.114 \cdot E_i$), and the over-compensated set (case 5, ln $A_i = 0.5 \cdot E_i - 67.49$), yield multi-peaked reaction rate curves, while the un-compensated set (case 3, $A_i = 10^{14}$ min^{-1}, $1 \leqslant i \leqslant 9$), yields a broad, effective reaction rate curve. For example, at 10 deg/min, over a 65° region, the reaction rates are within 97.5% of the maximum, which occurs at ~30% extent of reaction, indicating a supposed order of ~4.8. This case is similar to that discussed by the author [4], and considered too unrealistic. The two other models considered by Dowdy were devised to produce a maximum error, (case 8, positive, case 9, negative), between the Friedman-derived and the 'instantaneous mean' activation energies [7]. For case 8, the effective reaction exhibits one sharply defined maximum rate. The computed order decreases from 1.97 at 1 deg/min to 1.50 at 150 deg/min, and the Friedman-derived activation energies follow the same pattern as for the ten-member models with 10% incremental spacing, shown in Figure 6c. On

the other hand, for case 9, the reaction order is much larger. n increases from 3.15 at 1 deg/min to 4.19 at 150 deg/min. The Friedman activation energy pattern is closer to that shown for the fifty-member, 10% incrementally spaced model in Figure 6a.

Conclusions

The major contention of the original investigation [4], namely, that a set of mutually independent, first order reactions result in an effective n^{th} order reaction, has been confirmed. The single parameter selection and generation program, PARCAL, has proved very effective in enabling both symmetrical and skewed distribution models to be studied. Kinetic modelling with program KINMOD has shown that a singular n^{th} order overall reaction is only possible for an envelope of single reactions in which the extent of reaction of the last member, α_L, at the temperature of the maximum rate of the first reaction, is not less than 1% of α_1 at this temperature. The widest variation in the order of the overall reaction is obtained by selecting a skewed model which yields a set of decrementally spaced extent of reaction–temperature curves. Orders, varying from ~ 0.6 to ~ 3.0, can be obtained by appropriate selection of the number of members in the set, and change in relative spacing, a much wider range than hitherto proposed [4].

Friedman analysis of simulated non-isothermal reaction data is the preferred method for generating kinetic parameters, as previously emphasized [10]. For situations in which there is little variation in E_F, A_F values with extent of reaction, such as incrementally spaced models with only a small change in the relative spacing, or models involving only a limited number of members, generally ten or less, one obtains excellent agreement with Kissinger analysis-derived values, as previously demonstrated for single reactions, irrespective of the model [10]. Furthermore, for such models, Arrhenius analysis of single heating rate data, with tight control over the allowable deviations from linearity in the regression, can be performed over a wide range of the extent of the overall reaction. Many of the observations made in this study should be of interest, and hopefully assistance, to the experimentalist utilizing differential scanning calorimetry or thermogravimetry for the purpose of measuring kinetic parameters. Non-isothermal, multi-heating rate methods can be of great use, if carried out correctly. Kissinger analysis is useful in obtaining a quick measure of the activation energy and pre-exponential factor. Use of Friedman analysis is strongly advocated. The magnitude and direction of changes in the kinetic parameters, derived by this procedure, will assist the investigator in determining the possible complexity of the reaction studied.

Glossary of symbols

α	extent of reaction (dimensionless)
$d\alpha/dt$, $\dot{\alpha}$	rate of reaction (min^{-1})
T	absolute temperature (K)
E	energy of activation ($kJ \cdot mol^{-1}$)
$A \cdot T^m$	pre-exponential factor ($deg^{-m} min^{-1}$)
m	temperature exponent of pre-exponential factor
R	universal gas constant ($8.31434\ kJ \cdot mol^{-1} deg^{-1}$)
β	heating rate ($deg \cdot min^{-1}$; $K \cdot min^{-1}$)
$p_m(E/RT)$	general function including the exponential temperature integral
x, y, f, S_1, S_2	numbers descriptive of relative spacing between extent of reaction–temperature curves
L	numbers of members in a multiple reaction set
k_1, k_2	compensation law parameters

* * *

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Zusammenfassung — Es wird ein einfaches Verfahren beschrieben, mit dessen Hilfe ausgehend von einer breiten Vielzahl von Mehrfachreaktionen die Aktivierungsenergien und die präexponentiellen Faktoren der Teilreaktionen eines beliebigen kinetischen Modells erhalten werden können. Die Mehrfachreaktionen gehören zu drei Typen, bei denen die einzelnen Reaktionsgrad—Temperatur-Kurven bei einer bestimmten Temperatur divergieren, konvergieren oder äquidistant sind. Das Verfahren wurde an Reihen von Reaktionen erster Ordnung angewendet, bei denen die Gesamtreaktionsordnung n Werte zwischen 0.6 und 3.0 hatte. Abweichungen in den kinetischen Isokonversionsdaten nach Friedman weisen auf die Komplexizität der betrachteten Reaktionen hin.

Резюме — Посредством простого метода через энергии активации и предэкспоненциальные множители отдельных реакций, описана кинетическая модель, охватывающая широкий ряд многоступенчатых реакционных наборов. Эти наборы относятся к одному из трех классов, так что единственная мера реакции — температурные кривые — расходятся, сближаются или равномерно распределены по интервалам при одной предписанной температуре. Метод был применен к наборам реакций первого порядка и позволил получить эффективный n-ый порядок реакций с порядком "n", изменяющимся от ~ 0.6 до ~ 3.0. Изменения аналитических данных в изо-конверсионной реакционной кинетике Фридмэна служит признаком сложности решаемой реакции.